

Mechanochemical synthesis of Li–Mn–O spinels: positive electrode for lithium batteries

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Abstract

Li–Mn–O oxides were synthesized by mechanochemistry from a stoichiometric mixture of Li_2O and MnO_2 using various grinding times ($0 < t_{\text{milling}} < 15$ h). X-ray diffraction patterns of the ground samples ($t_{\text{milling}} < 10$ h) exhibit the same features as LiMn_2O_4 spinel structure (SG: $Fd\bar{3}m$) with, however, a slight discrepancy in the lattice parameter (a_{cub}) suggesting a non-stoichiometry of the Li–Mn–O oxides. a_{cub} increases with milling time to reach for 8 h of grinding a value of 8.24 \AA similar to stoichiometric LiMn_2O_4 . As a matter of fact, after 8 h of milling, mechanothesized Li–Mn–O spinel-type oxide shows quasi-identical electrochemical performances as high temperature LiMn_2O_4 ground for 1 h. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mechanochemistry; Grinding; Lithium manganese oxide; Electrochemistry; Lithium battery

1. Introduction

The spinel LiMn_2O_4 is of great interest for use in rechargeable lithium-ion batteries because of its high voltage, low cost, low stability and low toxicity [1]. For commercial applications, it is important to reach low temperatures at which a phase can be synthesized without affecting the electrochemical properties and to decrease the particle size to improve cell reversibility and capacity [2]. So, mechanochemistry, a low temperature method which allowing nanometers scale materials, was recently applied to electrode materials [3–5].

In this paper, the mechanochemical synthesis of Li–Mn–O spinels in relation with their electrochemical properties is reported. Comparison is being made between the effects of mechanical grinding on the structural and electrochemical properties of high temperature ceramic LiMn_2O_4 .

2. Experimental

The Li–Mn–O spinel-type oxides were synthesized both by mechanochemistry and by the “bake and shake” method.

Reagents of lithium salts (Li_2CO_3 , $\text{LiOH}\cdot\text{H}_2\text{O}$ or Li_2O) and manganese sources (MnO_2 -EMD) were used as starting materials. All the samples were prepared by reacting stoichiometric mixtures with $\text{Li}/\text{Mn} = 1/2$. Regarding the “bake and shake” method, the mixtures were heated at 800°C for 10 h in air. Concerning the second process, the lithium and manganese reactants mixture was directly ground in argon atmosphere, using a Spex 8000 mixer mill that generates normal mechanical strain [6], with various grinding times and a weight ratio of steel ball to powder of 28:1.

The final products were characterized by X-ray powder diffraction measurements using a Philips diffractometer PW 1710 with $\text{Cu K}\alpha$ radiation. A numerical method included in the DIFFRAC-AT software was used to obtain the position and the full width at half maximum (FWHM) of the diffraction peaks therefore allowing the identification of the solid phases and their state of division as a function of grinding time. The crystallite size was calculated from the Scherrer formula, which gives a rapid knowledge of the isotropic or anisotropic nature of the crystallite size sample. Multi-point Brunauer–Emmett–Teller (BET) surface area measurements were made using a Micromeritics Gemini II 2375 surface area. The powder morphology was studied as a function of milling time by scanning electron microscopy (SEM) with a Philips SEM model 505.

Electrochemical measurements were made using Swagelock™ cells. The positive electrode was prepared by mixing

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$\text{Li}_x\text{Mn-O}$ powder with 10 wt.% black carbon (SP), Li metal was used as negative electrode, and the electrolyte composition (1 M LiPF_6 dissolved in a 33/66 mixture of ethylene carbonate (EC) + dimethyl carbonate (DMC)) as the ionic conducting media. All the electrochemical tests were performed with a potentiostatic-mode coulometer on a MacPile Macintosh controlled (Bio-Logic, Claix, France) [7]. Cycling data were collected between 2.5 and 4.5 V at the rate of $C/10$. For simplicity, the starting composition (x) of $\text{Li}_x\text{Mn-O}$ materials was chosen equal to 1.

3. Results and discussion

Fig. 1 compares the XRD patterns of lithium manganese oxides prepared using a high temperature ceramic method (Fig. 1g) with mechanochemical synthesized oxides with various times of grinding (Fig. 1a–f). The ceramic material, identified as LiMn_2O_4 , crystallizes in a cubic structure (SG: $Fd\bar{3}m$).

For 1 h of grinding, the major peaks of a spinel-type phase are visible (Fig. 1b). Higher milling times lead to a better crystallization of the materials. The narrowing of the X-ray peaks (i.e. better crystallization) is correlated with an increase in the crystallite size, deduced using the Scherrer

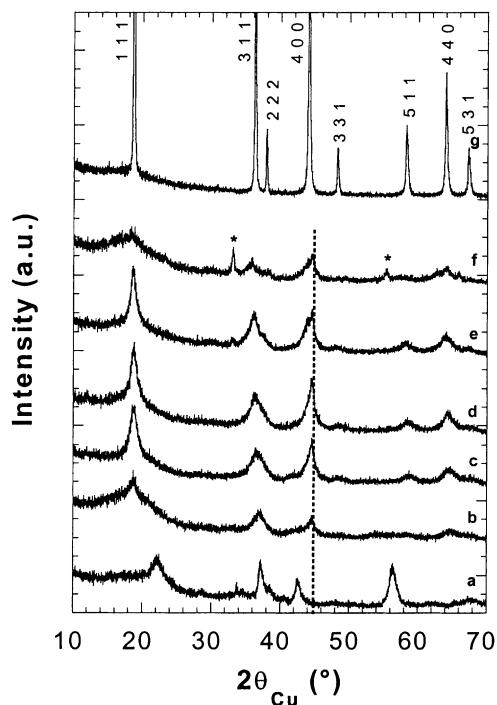


Fig. 1. X-ray diffraction patterns of $\text{Li}-\text{Mn}-\text{O}$ materials synthesized by mechanochemistry as a function of the grinding time: (a, b, c, d, e, f) samples ball-milled with the Spex for 0, 1, 3, 6, 8 and 15 h, respectively. For comparison, X-ray diffraction pattern of LiMn_2O_4 synthesized by ceramic method (Fig. 1g) is shown and indexed in the cubic system $Fd\bar{3}m$. The dotted line ($2\theta = 44.6^\circ$) reflects the presence of metallic iron (impurity due to the milling container). After 10 h of grinding, Mn_2O_3 (*) is present.

formula from the (1 1 1) X-ray peak, that varies from around 20 \AA after 1 h of grinding to 80 \AA after 8 h of grinding. As a general trend, the lattice parameter a_{cub} of the ground materials for milling time lower than 6 h, are slightly smaller than the one of the ceramic LiMn_2O_4 , suggesting a non-stoichiometry of the final material (a value of $8.19 (\pm 0.01) \text{ \AA}$ is calculated for the material ground 4 h compared to $8.24 (\pm 0.01) \text{ \AA}$ for the ceramic). The increase in lattice parameter with milling time suggests that the stoichiometry of the ground materials evolves upon grinding. Spinel compounds can be disordered, either through cation mixing (inverse spinel) or through cationic (or anionic) non-stoichiometry (deficient spinel). Thackeray et al. isolated two new deficient spinels in the $\text{Li}-\text{Mn}-\text{O}$ system, $\text{Li}_2\text{Mn}_4\text{O}_9$ and $\text{Li}_5\text{Mn}_4\text{O}_{12}$ [8]. Moreover, the X-ray pattern of the mechanothesized material, ground for 8 h, can be compared in X-ray peak position with the one of the high temperature ceramic LiMn_2O_4 ground for 1 h [9]. Further grindings (≥ 10 h) lead to an amorphization and a decomposition of the $\text{Li}-\text{Mn}-\text{O}$ spinel-type oxides, with the appearance of new phases mainly identified as Mn_2O_3 .

The X-ray evolution suggests a progressive reduction of the manganese oxidation state as well as a modification of the material stoichiometry upon grinding. A correlation may be made between milling effect (i.e. transfer of the mechanical energy into defects and heating) and synthesis temperature. Masquelier et al. reported that at low synthesis temperatures ($<400^\circ\text{C}$), deficient non-stoichiometric spinels, lying in the $\text{LiMn}_2\text{O}_4\text{--Li}_2\text{Mn}_4\text{O}_9\text{--Li}_4\text{Mn}_5\text{O}_{12}$ phase field, are stabilized, whereas at high temperatures, LiMn_2O_4 is synthesized [10].

The BET surface area fluctuates in the $12\text{--}18 \text{ m}^2/\text{g}$ range for any mechanochemically synthesized $\text{Li}-\text{Mn}-\text{O}$ sample. The fluctuations of BET surface correspond to the well-known welding-fracture equilibrium that takes place during milling [11]. A SEM microscopy study shows that the powders are formed of agglomerates of small particles, conglomerate ranging from 0.2 to $2 \mu\text{m}$. No spectacular changes in morphology are observable upon milling, however there is a slight tendency to agglomeration with higher milling times.

Fig. 2 shows the evolution of the voltage versus composition profiles of Li/LiPF_6 in EC/DMC/ $\text{Li}_x\text{Mn-O}$ cells versus grinding times of $\text{Li}-\text{Mn}-\text{O}$ materials. Whatever the time of milling, all curves exhibit a high polarization that may be partly attributed to the small particle size (i.e. large specific surface area) of ground materials. Regarding the shape of the voltage–composition curve, Fig. 2 can be divided in three parts: low milling time (<3 h), high milling time (>15 h), and intermediate milling times.

Fig. 2a shows a rather linear evolution of the voltage versus composition for the poorly crystallized material ground for 1 h. Upon milling (<15 h), two distinct voltage domains centered around 3 and 4 V appear (Fig. 2b–d). The non-appearance of two plateaus as for the ceramic sample may come from the non-stoichiometry (oxygen

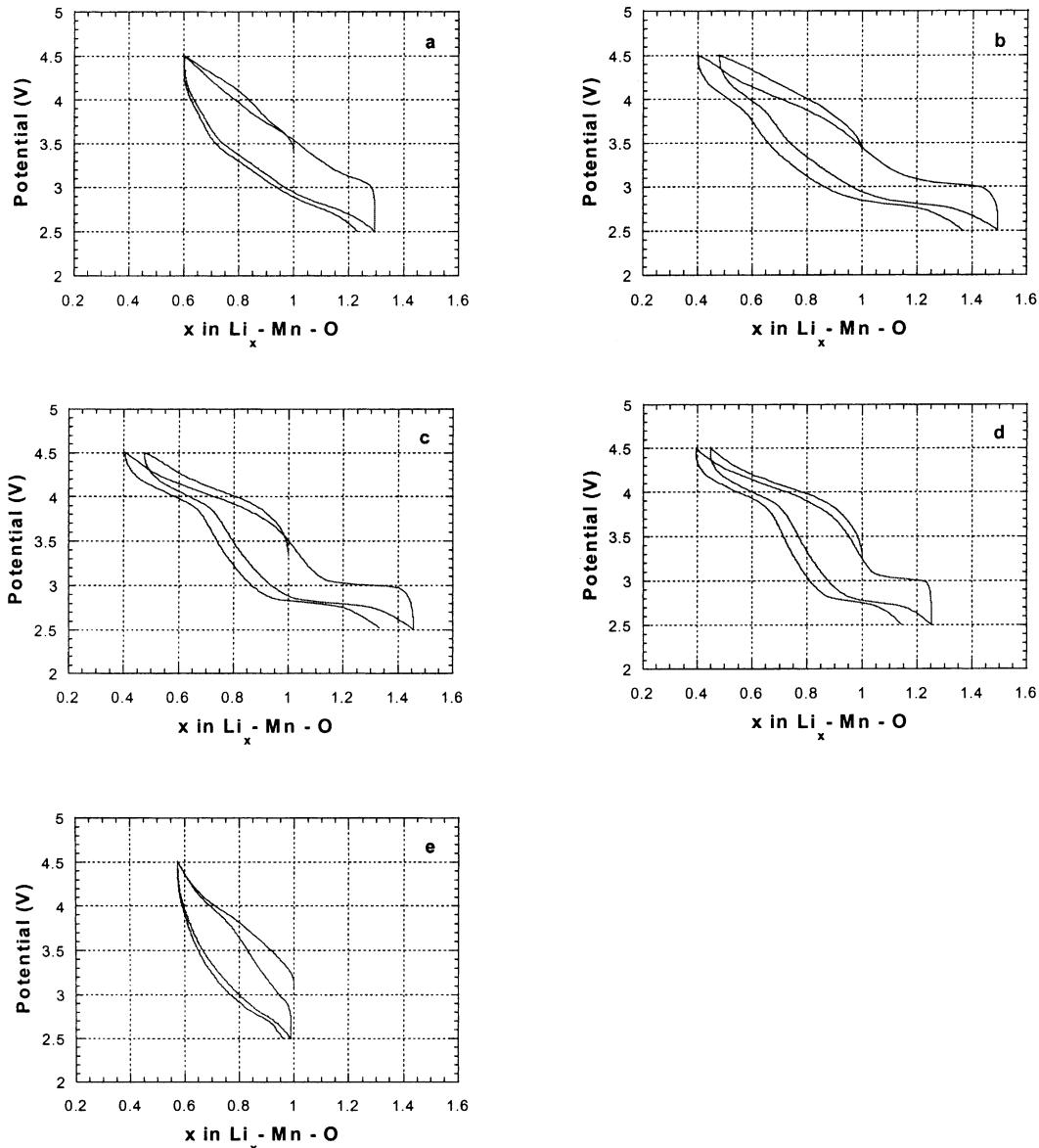


Fig. 2. Voltage vs. composition curves (a, b, c, d, and e) of cells using $\text{Li}_x\text{-Mn-O}$, prepared by ball milling of $\text{Li}_2\text{O} + \text{MnO}_2$ for 1, 3, 6, 8, and 15 h, respectively. (Cycling rate: C/10).

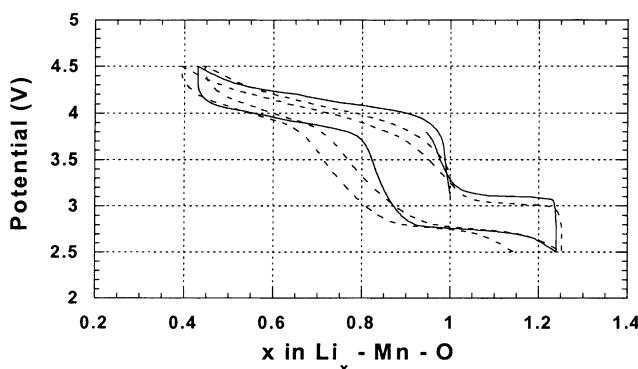


Fig. 3. Comparison between the voltage vs. composition curve of $\text{Li}_x\text{-Mn-O}$ for material mechanochemically ground for 8 h (dotted lines) and LiMn_2O_4 ceramic material ground for 1 h (continuous line).

deficiency, $\text{Li}/\text{Mn} \approx 1/2$), poor crystallinity, and disordered character of ground $\text{Li}_x\text{-Mn-O}$ spinel materials. Indeed, for 8 h of grinding the voltage–composition curve become close to that of the ceramic LiMn_2O_4 material ground for 1 h (Fig. 3) [9].

For higher milling times (Fig. 2e), the electrochemical performances decreases, in relation with a progressive decomposition of the ground material (Fig. 1).

4. Conclusion

In summary, $\text{Li}-\text{Mn-O}$ spinel-type oxides were synthesized by mechanochemistry, from a stoichiometric mixture of Li_2O and EMD- MnO_2 . X-ray patterns of the ground

materials are identified as LiMn_2O_4 spinel structure with, however, a slight discrepancy in the lattice parameter (a_{cub}) suggesting a non-stoichiometry of the Li–Mn–O oxides. After 8 h of grinding, the mechanochemical synthesized material exhibits structural and electrochemical characteristics similar to the 1 h ground high temperature ceramic LiMn_2O_4 .

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